

OFFICE OF NAVAL RESEARCH
END-OF-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

N00014-95-1-0306

The Reactivity and Dynamics of Gaseous Clusters
Subtitle: The Dynamics and Controlled Shaped Synthesis of Gaseous and Colloidal
Nanoparticles

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October, 1997

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4131015
Contract/Grant Number: N00014
Contract/Grant Title: The Reactivity and Dynamics of Gaseous Clusters
Principal Investigator: M. A. El-Sayed
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Georgia Institute of Technology
Atlanta, GA 30332-0400

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E-mail Address: mostafa.el-sayed@chemistry.gatech.edu

- a. Number of papers submitted to refereed journals, but not published: 1
b. +Number of papers published in refereed journals (for each, provide a complete citation): 5
c. Number of books or chapters submitted, but not yet published: 0
d. +Number of books or chapters published (for each, provide a complete citation): 1
e. +Number of printed technical reports/non-refereed papers (for each, provide a complete citation): 0
f. Number of patents filed: 1
g. +Number of patents granted (for each, provide a complete citation) 0
h. +Number of invited presentation (for each, provide a complete citation): 0
i. +Number of submitted presentations (for each, provide a complete citation): 0
j. +Honors/Awards/Prizes for contract/grant employees (list attached):
(This might include Scientific Society Awards/Offices, Selection as Editors, Promotions, Faculty Awards/Offices, etc.)
k. Total Number of Full-Time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
Graduate Students: 2
Post-Doctoral Associates: 0
Including the number of,
Female Graduate Students: 1
Female Post-Doctoral Associates: 0
the number of
Minority* Graduate Students: 1
Minority* Post-Doctoral Associates 0
and the number of
Asian Graduate Students: 0
Asian Post-Doctoral Associates: 0
l. +Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant).

+Use the letter and an appropriate title as a heading for your list, e.g.:

- b. Published Papers in Refereed Journals, or d. Books and Chapters published
Also submit the citation lists as ASCII files, preferably on a 3" or 5" PC-compatible floppy disk.

*Minorities include Blacks, Aleuts, Amindians, Hispanics, etc. NB? Asians are not considered an under-represented or minority group in science and engineering.

Part 1

a. Papers Accepted or Submitted to Refereed Journals (and not yet Published)

1. S.L.Logunov, R. Little and M. A. El-Sayed, "Quantum Well Confinement Effects on the Nonradiative Relaxation Process of Quantum Dots", J.Phys.Chem. Submitted for publication.

b. Papers Published in Refereed Journals

1. Temer S. Ahmadi and Mostafa A. El-Sayed, "Effect of Lattice Energy Mismatch on the Relative Mass Peak Intensities of Mixed Alkali Halide Nanocrystals", J.Phys.Chem.A, **101** (4) 690-693 (1997)
2. Li Song, M. A. El-Sayed, and Peter C. Chen, "Spectral diffusion within the porous silicon emission wavelength range on the nanosecond to millisecond time scale", J.Appl.Phys. **82** (2) 836-839 (1997)
3. L.Cai, A. Rohatgi, D. Yang, M. A. El-Sayed, "Effects of rapid thermal anneal on refractive index and hydrogen content of plasma-enhanced chemical vapor deposited silicon nitride films", J.Appl.Phys. **80** (9), 5384-5388 (1996)
4. S.L. Logunov, T. S. Ahmadi, M. A. El-Sayed, J. T. Khoury, R. L. Whetten, "Electron Dynamics of Passivated Gold Nanocrystals Probed by Subpicosecond Transient Absorption Spectroscopy", J.Phys.Chem.B. **101** (19) 3713-3719 (1997)
5. Z.L. Wang, T. S. Ahmadi, M. A. El-Sayed, "Steps, ledges and kinks on the surfaces of platinum nanoparticles of different shapes", Surface Science, **380**, 302-310 (1997)

c. Books or Chapters Submitted but not yet Published

None

d. Books or Chapters Published

One

e. Technical Reports Published

None

f. Patents Filed

Synthesis of Shape Controlled Platinum Nanoparticles

g. Patents Granted

None

h. Invited Presentations

1. July 21-26, 1996. IVI IUPAC Symposium on Photochemistry, Helsinki. "On the Molecular Origin of the Protein Catalysis of the Primary Process in Bacteriorhodopsin Photosynthesis: Retinal Photoisomerization". (Invited Speaker)
2. September 8-12, 1996. Nobel Symposium on Femtochemistry and Femtobiology Ultra Fast Reaction Dynamics at Atomic Scale Resolution". (Invited Speaker)
3. September 16-19, 1996 2nd International Conference on Lasers, Cairo. "Femtosecond Lasers and the Study of the Primary Ultra Fast Processes in Photochemistry and Photobiology". (Invited Speaker)
4. January 1-6, 1997 4th International Conference and Workshop on Solar Energy Storage and Applied Photochemistry, Cairo, Egypt. "The Molecular Mechanisms of the Primary Processes of the other Natural Photosynthetic System" (Invited Speaker)
5. January 4-9, 1997 4th International Conference on Frontiers of Polymers and Advanced Materials, Cairo, Egypt. "Shape and Surface Coverage Dependence of the Catalytic and Dynamic Properties of Nanoparticles" (Chairman, Intl. Program Committee, Invited Speaker)
6. March 22, 1997 The Okazaki Conference, "Nanoparticles, A New State of Matter", Okazaki, Japan (Invited Speaker)
7. March 24, 1997 Hong Kong University, Hong Kong (Invited Speaker)
8. April 8, 1997 University of Florida, Gainesville, FL (Invited Speaker)
9. April 14, 1997 ACS Conference, Division of Physical Chemistry Meeting, "Metallic Nanoparticles with Different Shapes", San Francisco, CA (Invited Speaker)
10. April 15, 1997 ACS Conference, Division of Colloidal and Surface Chemistry Meeting, "Quantum Well Confinement in Semiconductor Nanoparticles", San Francisco, CA (Invited Speaker)
11. April 22, 1997 Nobel Selection Committee, "Report to the Nobel Committee - Femtosecond Chemistry (Femtochemistry)", Stockholm, Sweden (Invited Speaker)
12. July 11, 1997 Wolf Symposium, "From Molecular Crystals to Molecular Electronics", Munich, Germany (Invited Speaker)
13. July 21-25 Gordon Conference, R.I. (Invited Speaker)
14. July 31, 1997 Rohm and Haas, "Nanocrystals & Ultrafast Dynamics", Spring Hill, PA (Invited Speaker)
15. September 15, 1997 Texas A&M, "Bacteriorhodopsin: The Dynamics of the primary process: The retinal photoisomerization", College Station, TX (Invited Speaker)
16. September 16, 1997 Texas A&M, "Bacteriorhodopsin: The Metal Cation Binding Sites", College Station, TX (Invited Speaker)

17. September 17, 1997 Texas A&M, "Metallic and Semiconductor Nanoparticles: Structure and Dynamic Studies", College Station, TX (Invited Speaker)

I. Submitted Presentation

None

j. Honors/Awards/Prizes

Lind Lecturer, Oak Ridge National Laboratory, Oak Ridge, TN
Member of the Comstock Prize Committee, National Academy of Sciences
Member of the International committee to propose change to IUPAC
The Frontier Lecturer, Texas A&M
Nobel Symposium on Femtochemistry, Speaker of the closing session

k. Number of Full-time equivalent Graduate Students and Post-Doctoral Associates supported during this period under this grant number.

Total	<u>2</u>	Postdoctoral	<u>0</u>
Female Graduate Students	<u>1</u>	Female Postdoctoral	<u>0</u>
Minority Graduate Students	<u>1</u> (AfricanAmerican)	Minority Postdoctoral	<u>0</u>
Asian Graduate Students	<u>0</u>	Asian Postdoctoral	<u>0</u>

1. Other Funding

1. DOE - "Time Resolved Laser Studies on the Proton Pump Mechanism of Bacteriorhodopsin" \$135,000 9/1/97-8/30/98
2. NSF - "Real Time Clocking of Energy Redistribution in Molecules Falling Apart" \$90,000 3/1/96-2/29/97 (No renewal is intended; instead a new proposal is pending on catalysis using metallic nanoparticles of different shapes)

Part II

- a. Principal Investigator: Professor M. A. El-Sayed
- b. Current telephone number: (404)894-0292
- c. Cognizant ONR Scientific Officer: Dr. Peter Schmidt
- d. Brief description of project:

In order to design new strategic materials with specific properties, we need to understand the binding forces that exist in mixed atoms or molecules not present in conventional material. Thus our aim is to understand the adhesive and cohesive forces holding atoms or molecules together in unconventional nanoparticles that do not usually bind together in conventional macroscopic materials. In the broad sense, we like to understand these forces by studying the structure, stability, and the dynamic process of the rapid electronic motion in nanoparticles. Due to the large surface to volume ratio, these particles tend to have different properties not present in the bulk nor of the individual atoms or molecules making these nanoparticles. Thus they offer us an opportunity to unravel new properties with new potential applications.

The aim of our present research is to synthesize and study the forces between atoms or molecules within metallic and semiconductor nanoclusters. These forces determine the dynamic properties and thus the potential uses of the nanoparticles. In the past several years, we have confined our studies to gaseous clusters and studied the dynamics of their dissociation and their chemical reactivities. During the past couple of years (since we have moved to Georgia Tech), we have expanded our activity to include the synthesis and study of the dynamics of excitation relaxation in colloidal nano-particles, both semiconductor and metallic. The forces that control the shapes of nanoclusters by capping agents are to be examined. The synthetic method we use involves a competition between nucleation of the atoms in the metallic nanoparticles or the semiconductor molecules in the semiconductor nanoparticle and the capping process of the surface with polymeric molecules. The faster the capping process, the smaller would be the average size of the clusters formed.

The expansion in our research activity over the last couple of years has resulted from our move to Georgia Tech where we found an excellent TEM facility that enabled us to

determine the structures of the nanoparticles synthesized in solution. Having built the Laser dynamics Laboratory here at Georgia Tech, we began to study the ultrafast dynamic properties of the electrons and the holes in metallic and semiconductor nanoparticles.

e. Significant Results During Last Year:

1) Dependence of the Stability of Gaseous Mixed Clusters on the Lattice Energy Mismatch (VG_1 , VG_2 , VG_3)

We determined the relative intensity of the different mass peaks for alkali halide mixed clusters with magic number of total number of molecules in the cluster of 13 having the formula $M_1 (M_{1(13-n)} M_{2(n)} X_{13})^+$, where M_1 and M_2 are two different alkali metal ions and X is a halide ion. We selected metal halides of comparable lattice energies (e.g. RbI and KI) and of different lattice energies (e.g. NaI, KI, or RbI). The results for the former are shown in V_1 and those for the latter are shown in VG_3 . For a cluster of fixed number of M_1X and M_2X (giving rise to one mass peak), a number of isomers, resulting from the relative position of the two molecules, contribute to the intensity of its mass peak. When the energy mismatch is small (VG_1), the miscibility of one into the other is continuous and the statistical number of isomers contributing to each mass peak determines its relative intensity as shown in VG_2 . For clusters of mixed salts of large lattice energy mismatches, it was difficult to observe mass peaks for compositions in which more than three molecules of one salt dissolves into the other salt. This suggests that the misfit in lattice energy and ionic radii give rise to unstable clusters which leads to rapid rate of cluster evaporation and unobserved cluster mass peaks.

2) The Detailed Structure of Individual Platinum Metallic Nanoparticles: (VG_4 , VG_5 , VG_6 , VG_7)

In our previous gas phase studies, the clusters were identified only by their mass peak position. While this identification is useful in determining relative stabilities and kinetic related studies, it gives no satisfaction as one does not know how they look.

At Georgia Tech, there is the High Resolution Transmission Electron Microscopic (HRTEM) facility that can resolve structures on atomic resolution. We have examined the detailed structures of the platinum nanoparticles that we have reported to synthesize in our last year report. VG_4 and VG_5 show the detailed structures of a cubic particle oriented along different faces. VG_6 shows the images of tetrahedral-like particles and VG_7 shows that of an octahedral-like particle. In all these particles, one can see the structure of each particle with each having different types of defects and different degree of roughness as well as different truncation at corners or edges giving rise to different facets.

3) Quantum Well Confinement Effect on the Rate of Nonradiative Processes of Semiconductor Dots: (VG_8 , VG_9 , VG_{10})

Reducing the size of a semiconductor particle below its exciton Bohr radius leads to quantum confinement effects. Decreasing the size of these particles leads to large changes in their properties, like increasing their band gap, their absorption intensity, their cross-sections of nonlinear processes and increasing the probability of their surface trapping due to increase in their surface to volume ratios.

Recently, Weller et al showed that particles can be synthesized in which the nanoparticle core (e.g. CdS) can be covered by one shell of HgS which is also capped with one shell of CdS. Since HgS has a much smaller band gap than CdS, it will act as a trap (quantum well) for the excited electron and hole. Indeed, it has been shown that the emission results from recombination of the trapped electron and hole in the well rather than on the surface as seen in CdS quantum dots (QD).

We compared the rate of the nonradiative energy relaxation of high energy excitons in both the CdS:HgS:CdS quantum dot quantum well (QDQW) and CdS QD. VG_8 shows the time behavior of an optical hole, oh, (absorption bleach) we induced at 400 nm in a colloidal solution of each system. In the QD (VG_8 -A), no oh is observed between excitation and the band gap (the lowest energy absorption region) while in the QDQW system (VG_8 -B), we see spectral diffusion with time from the low energy side of excitation toward the band gap absorption. Furthermore, the derivative of the spectrum shown in VG_8 -B gives two peaks shown in VG_9 inset. These peaks correspond to different calculated (Bryant, Phys.Rev) energies of the electron and hole in the QDQW. VG_{10} shows the time dependence of the dynamics (the rise and decay) of the relaxation process which is shown to depend on the energy range in which peak the rates of the dynamics of the excited electron and hole are measured. Thus the rise and decay of the bleach recovery is faster in the 490-530 nm range than in the 630-660 nm range. This suggests that the spectral diffusion is due to relaxation between the excited state in the QDQW cluster.

This means that the relaxation of high energy excitons in QDQW is slower than that in the QD by 3-4 orders of magnitude. We have proposed to explain this in terms of the large difference in the energy spacing between the excited states of the two systems. According to Bryant, the energy level calculations have shown that the average energy spacing in the QDQW is 1600 cm^{-1} while in the QD it is only 480 cm^{-1} . Thus compared to phonon frequencies ($\sim 300\text{ cm}^{-1}$), the rate of electron-hole phonon relaxation in the QD is

expected to be much faster than in QDQW. This is an interesting new property of Quantum Confinement in these nanoparticles. It should be mentioned that if the energy gap of the well material is not much smaller than that of the core, such large confinement would not have been observed! We are presently studying this confinement as a function of the relative band gap energies of the well and the core. The effect of having the middle semiconductor layer process larger band gap (thus acting as a quantum barrier instead of a well) is also being studied.

f. Proposed Work for Next Year

See Renewal Proposal

G. Graduate Students and Postdoctoral Fellows

50% of two graduate students, Reginald Little (African American) and Travis Green. 50% of a postdoctoral fellow (Dr. Stephan Logunov). The other 50% of the stipend of the students was supported by MDI.

PART III. Summary of Work Published Last Year

1. Temer S. Ahmadi and Mostafa A. El-Sayed, "Effect of Lattice Energy Mismatch on the Relative Mass Peak Intensities of Mixed Alkali Halide Nanocrystals", *J. Phys. Chem.*, **101**, (4), 690-693 (1996)

The relative mass peak intensity distribution of the $[M_{14}A_{13}]^+$ mixed alkali halide nanocrystals containing a "magic" number of 14 metal cations (M and A) and 13 iodide anions is examined. These nanocrystals were generated through sputtering of mixed solid alkali halides using fast atom bombardment and analyzed by use of a double-focusing sector field mass spectrometer. The mass peak intensities of mixed cluster ions composed of two different metals relative to the "pure" nanocrystals (containing one or the other metal) are compared for two types of mixed cluster ions: one with small lattice energy mismatch, i.e. $[Rb_{14}K_{13}]^+$ cluster ions, and the other type with large lattice energy mismatch, i.e., $[Cs_{14}A_{13}]^+$ cluster ions where A is either Na, K, or Rb. In contrast to what was previously found for clusters with small energy mismatch in which the rate of *formation* (which depends on the possible number of isomers that each mixed cluster ion can have) determines the relative intensities of mass peaks, the rate of *evaporation* (i.e., the cluster instability) determines the relative mass peak intensities in salts with relatively large lattice energy mismatch. These results are consistent with our previously proposed kinetic model for the formation and decay of these clusters.

2. Li Song and M. A. El-Sayed, "Spectral diffusion within the porous silicon emission wavelength range on the nanosecond to millisecond time scale", *J. Appl. Phys.*, **82**, (2), 836-839 (1997)

The emission spectrum from porous silicon (PS) at room temperature was recorded after different delay times ranging from 30 ns to 2.0 ms after pulsed laser excitation by using a gated charge-coupled device camera. In agreement with previous studies, the photoluminescence of porous silicon was found to redshift with delay time in the ns to 100 μ s time scale. However, a study of the normalized band shape of the redshifted emission reveals that the emission spectrum retains its band shape rather than giving a distorted band shape that increases in intensity on the longer wavelength side. This behavior suggests that the redshift in the emission spectrum of porous silicon is a result of spectral diffusion resulting from energy transfer among emitters within the inhomogeneously broadened absorption spectrum. Furthermore, on the longer time scale (0.8-2 ms), the much weaker, long wavelength emission spectrum is found to blueshift as the delay time is increased. Two peaks were resolved in the photoluminescence spectrum. One is centered around 650 nm and the other is centered around 750 nm. The photoluminescence at 600 and 800 nm have lifetimes of 0.35 and 0.19 ms, respectively. This observation suggests the existence of two distinct molecular species responsible for the observed photoluminescence in PS. © 1997 *American Institute of Physics*. [S0003-6951(97)01025-5] 78.55.Mb, 78.55.Ap

3. L. Cai, A. Rohatgi, D. Yang and M. A. El-Sayed, "Effects of rapid thermal anneal on refractive index and hydrogen content of plasma-enhanced chemical vapor deposited silicon nitride films", *J. Appl. Phys.*, **80**, (9), 5384-5388 (1996)

The objective of this paper is to understand and quantify the effects of rapid thermal anneal (RTA) on refractive index, thickness, and hydrogen content of plasma-

enhanced, chemical vapor-deposited (PECVD) silicon nitride films. It is shown that RTA is more effective than identical furnace anneal. A threshold in as-deposited refractive index value is found, above which the index of a silicon nitride film increases, while the thickness and bonded hydrogen content decreases as result of the RTA. In addition, the magnitude of increase in the index is proportional to the as-deposited index value. The threshold index value increases with the increase in silicon nitride deposition temperature. A Direct correlation is found between the annealing-induced increase in refractive index and the corresponding decrease in total bonded hydrogen concentration in the PECVD silicon nitride films. Finally, it is shown that the release of bonded hydrogen from the film can passivate defects in the underlying silicon substrate and increase the performance of silicon devices such as solar cells. © 1996 *American Institute of Physics*. [S0021-8979(96)08621-5]

4. S.L. Logunov, T. S. Ahmadi, and M. A. El-Sayed, "Electron Dynamics of Passivated Gold Nanocrystals Probed by Subpicosecond Transient Absorption Spectroscopy", *J.Phys. Chem.*, **101**, (19), 3713-3719 (1997)

The electronic dynamics of gold nanocrystals, passivated by a monolayer of alkylthiol (ate) groups, were studied by transient spectroscopy after excitation with subpicosecond laser pulses. Three solution-phase gold samples with average particle size of 1.9, 2.6, and 3.2 nm with size distribution less than 10% were used. The photoexcitation in the intraband (surface plasmon region) leads to the heating of the conduction electron gas and its subsequent thermalization through electron-electron and electron-phonon interaction. The results are analyzed in terms of the contribution of the equilibrated "hot" electrons to the surface plasmon resonance of gold. A different spectral response was observed for different sizes of gold nanoparticles. The results were compared to the dynamics of the large (30 nm diameter) gold nanocrystals colloidal solution. The size-dependent spectral changes are attributed to the reduction of the density of states for small nanoparticles. The observed variation in the kinetics of the cooling process in gold nanoparticles with changing the laser intensity is attributed to the temperature dependence of the heat capacity of the electron gas.

5. Z.L. Wang, T. S. Ahmadi, M. A. El-Sayed, "Steps, ledges and kinks on the surfaces of platinum nanoparticles of different shapes", *Surface Science*, **380**, 302-310 (1996)

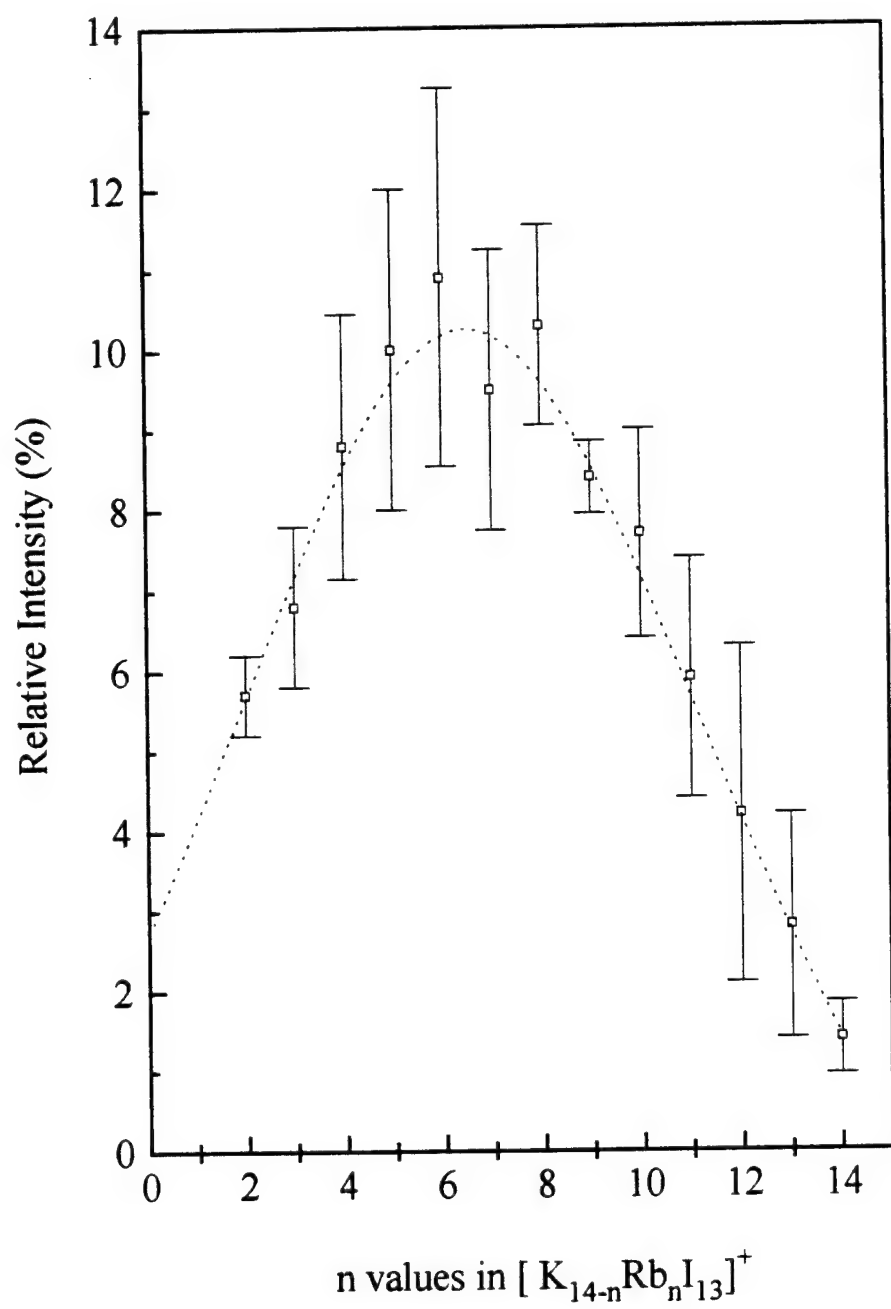
Platinum nanoparticles with a high percentage of cubic-, tetrahedral-, and octahedral-like shapes, respectively, have been synthesized by a shape-controlling technique that we developed recently [Ahmadi et al., *Science* 272 (June 1996) 1924]. High resolution transmission electron microscopy (HRTEM) is used here to directly image the atomic scale structures of the surfaces of these particles with different shapes. The truncated shapes of these particles are mainly defined by the {100}, {111}, and {110} facets, on which numerous atom-high surface steps, ledges and kinks have been observed. This atomic-scale fine structure of the surfaces of these particles is expected to play a critical role in their catalytic activity and selectivity. © 1997 Elsevier Science B.V.

VIEWGRAPHS

VG₁ to VG₁₀

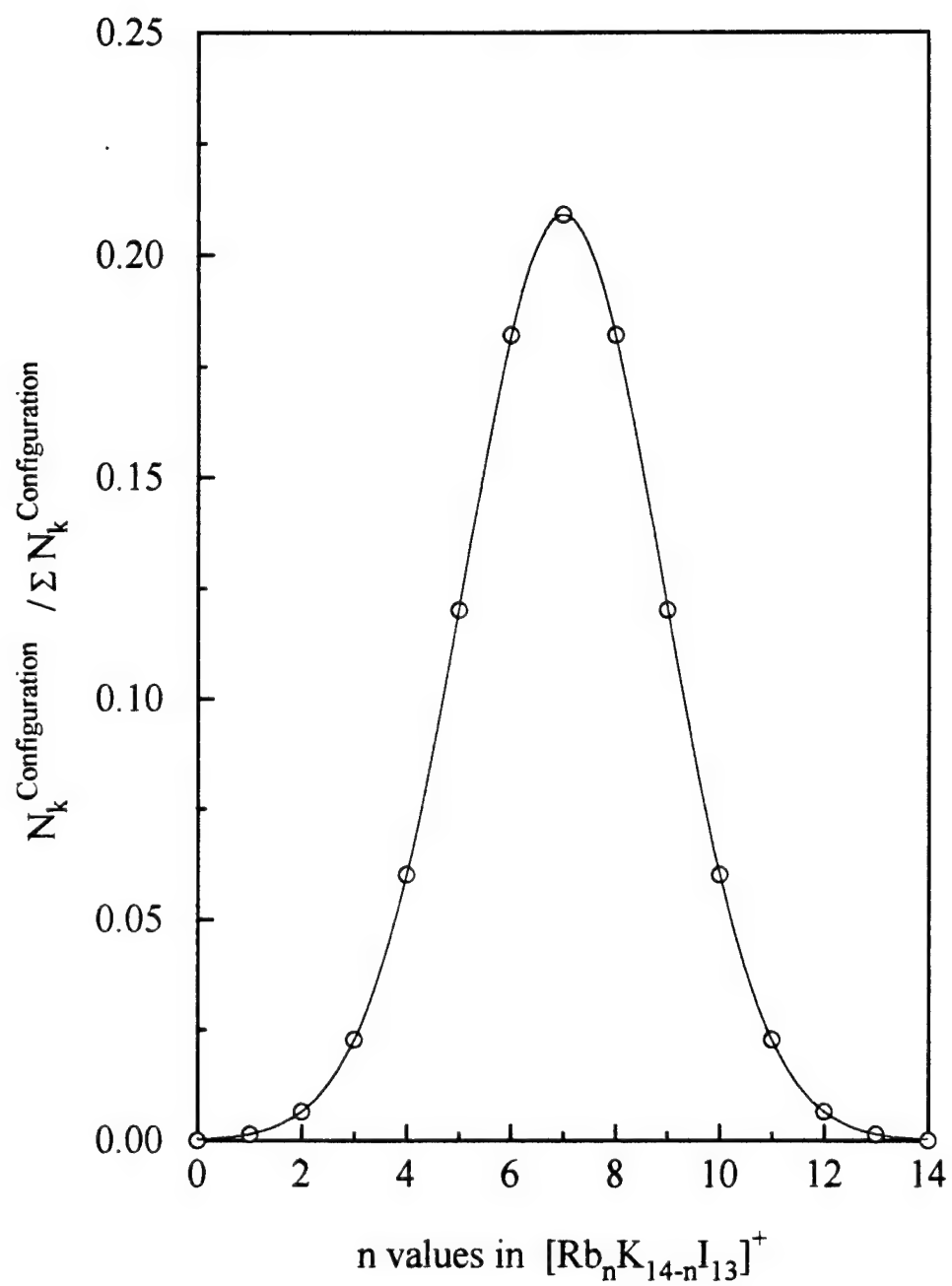
VG₁: STABILITY OF GASEOUS MIXED CLUSTERS: small lattice energy mismatch.

The calculated relative intensities of mixed-nanocrystals of $[\text{Rb}_n\text{K}_{14-n}\text{I}_{13}]^+$ made of KI and RbI whose lattice energies are comparable. The relative intensities were normalized with respect to the total sum of the intensities of the individual ions.



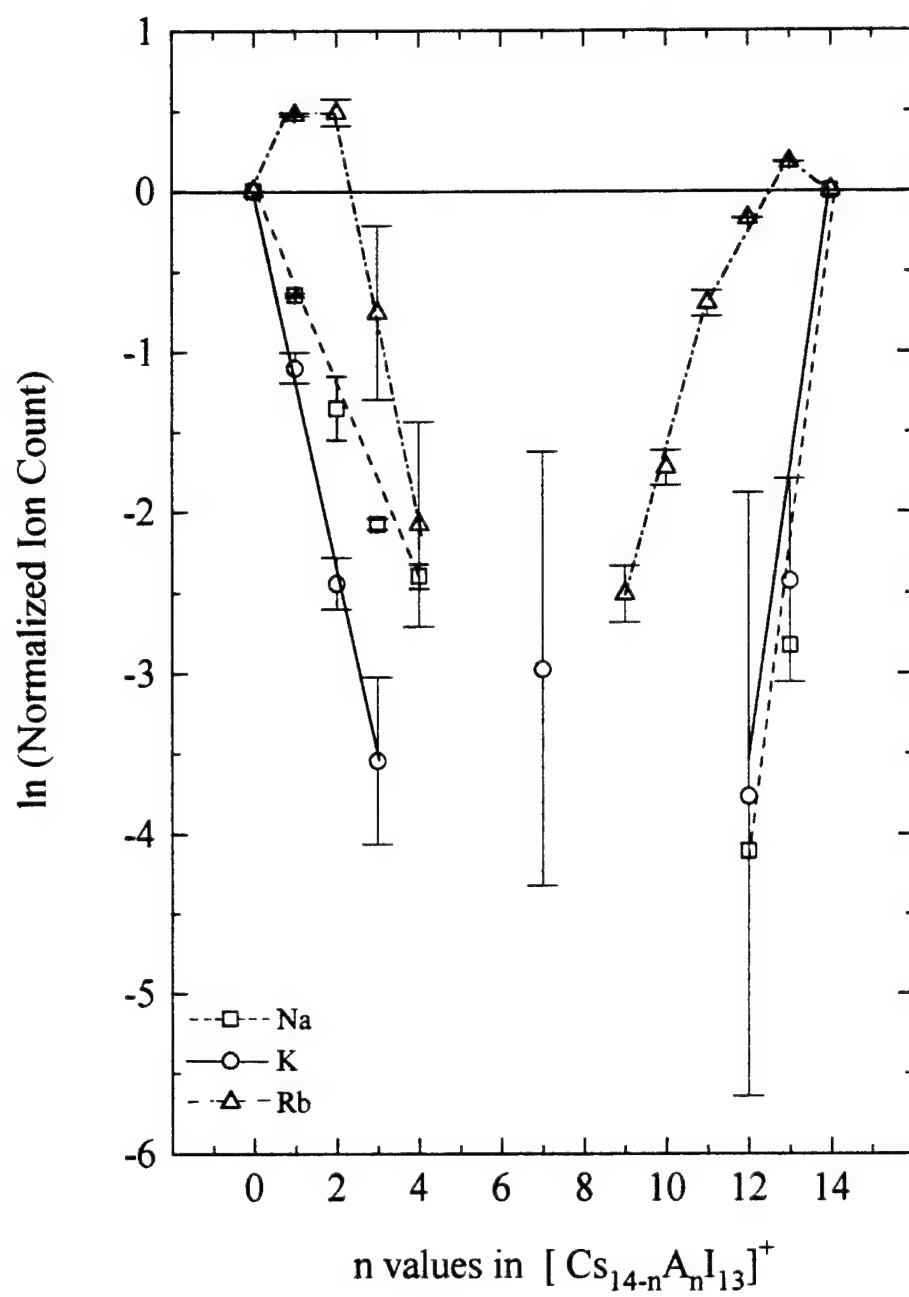
VG₂: NUMBER OF ISOMERS AND MASS-PEAK INTENSITIES

The predicted dependence of the relative number of isomers of the mixed-nanocrystals on their composition, i.e. the number of KI and RbI molecules. A mixed-nanocrystal of $[\text{Rb}_n\text{K}_{14-n}\text{I}_{13}]^+$ having equal number of K^+ and Rb^+ ($n=7$) has the largest relative number of isomers. This strongly suggests that in case of mixed clusters of components with small energy mismatch, the statistical number of isomers present for each cluster determines the stability of the cluster and its relative mass peak intensity.



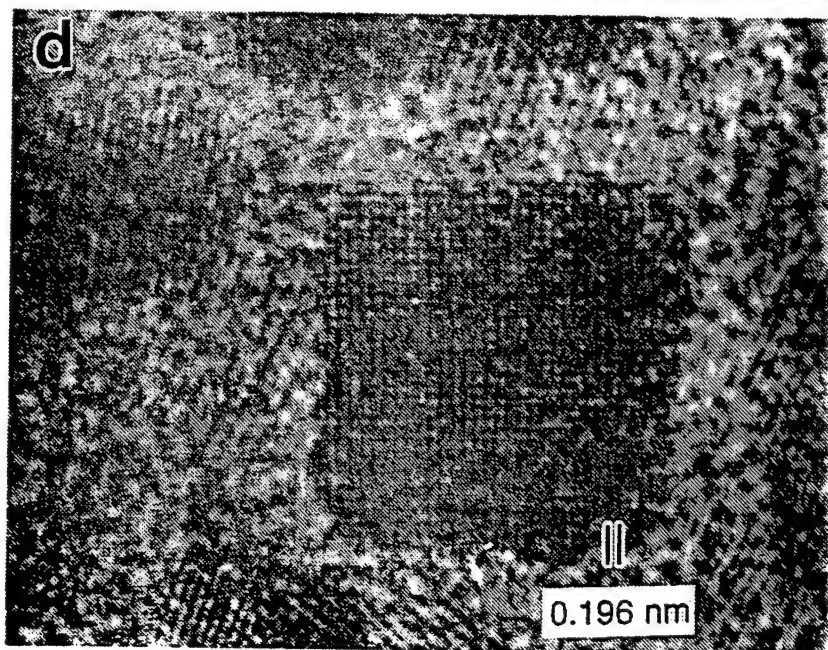
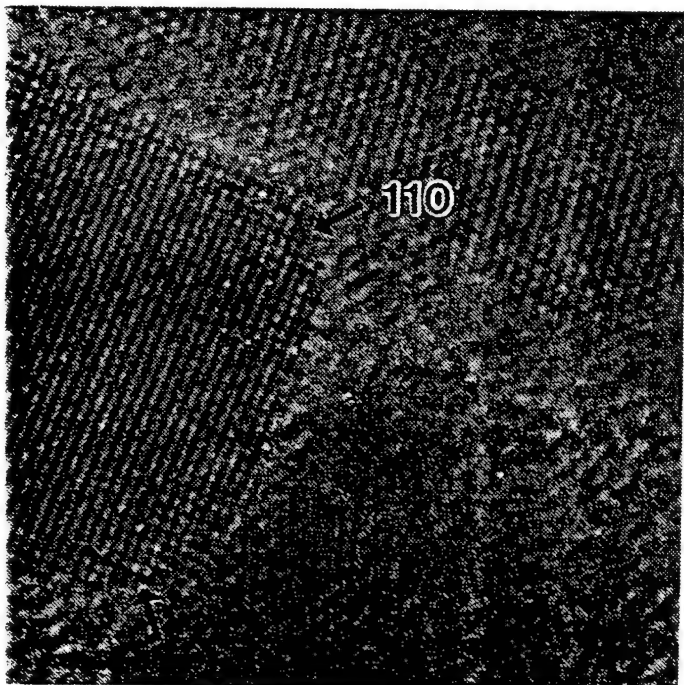
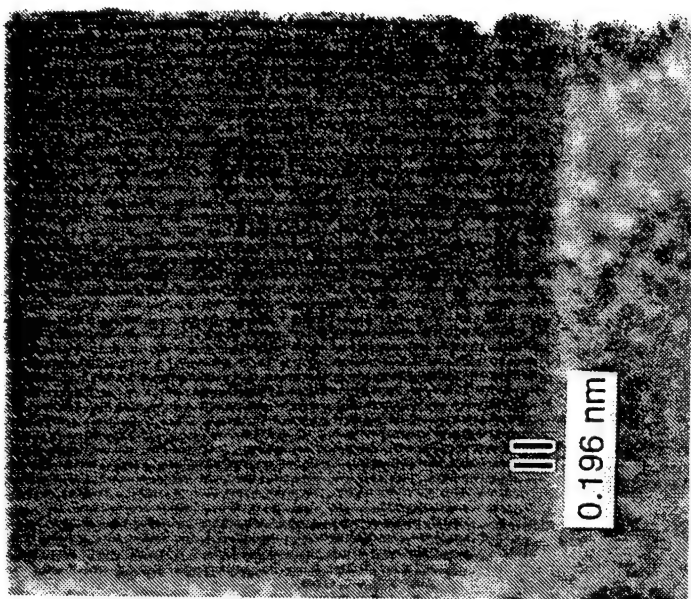
VG₃: STABILITY OF GASEOUS MIXED CLUSTERS: CASE OF LARGE ENERGY MISMATCH

The calculated relative intensities of mixed -nanocrystals of $[\text{Cs}_{14-n}\text{A}_n\text{I}_{13}]^+$ where A designates either Na (squares), K (circles) or Rb (triangles) from their observed mass spectrum. The intensities are plotted as \ln (relative ion count) against n values. The intensities were normalized with respect to $[\text{Cs}_{14}\text{I}_{13}]^+$. No peaks are observed for mixed clusters with large number of one molecule mixed with the other due to great instability resulting from the large mismatch in lattice parameters.



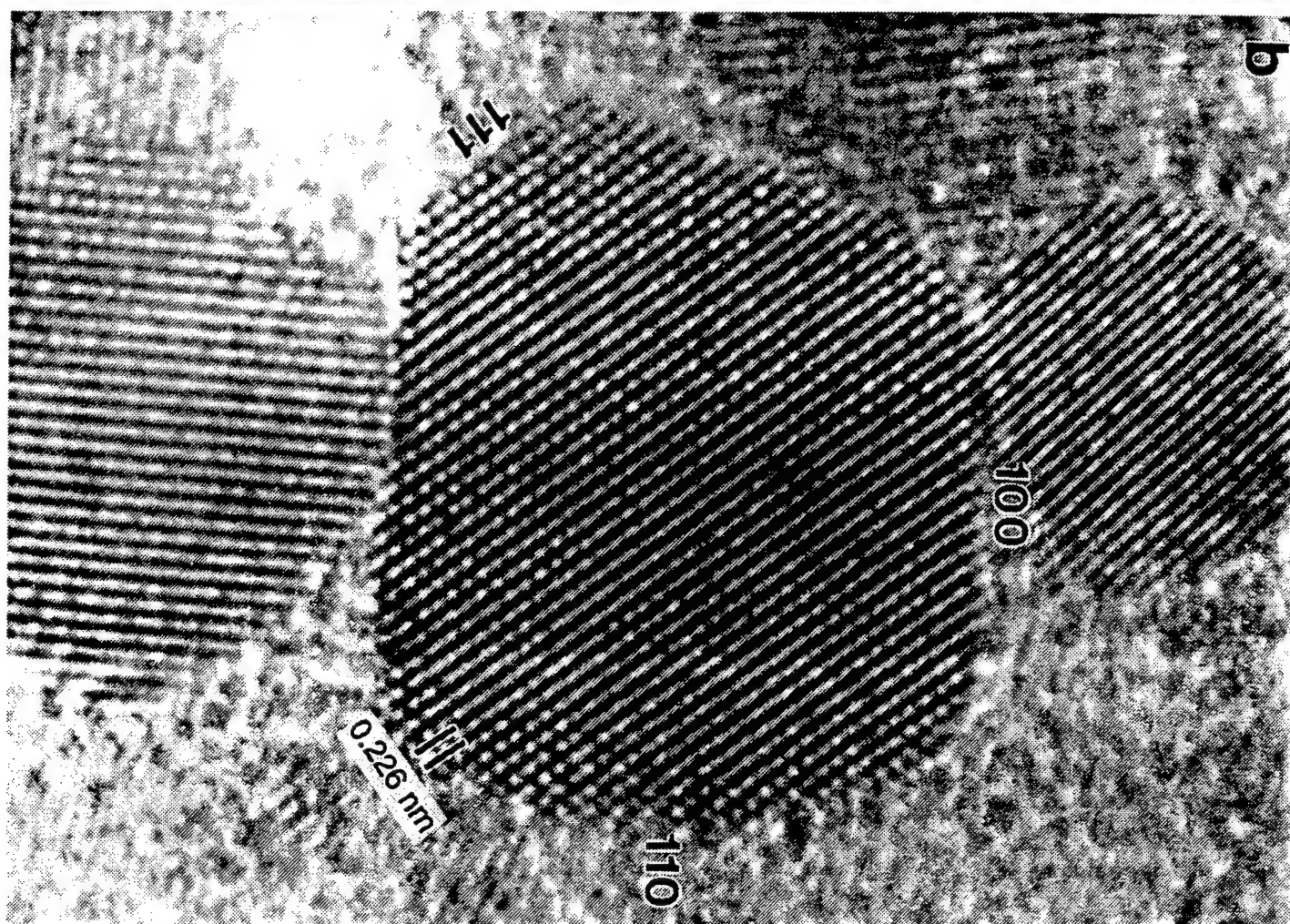
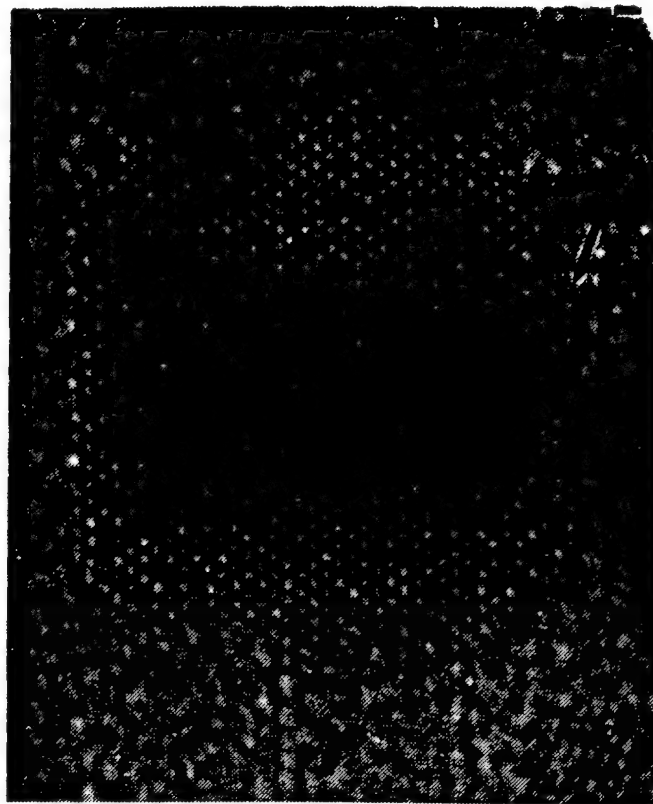
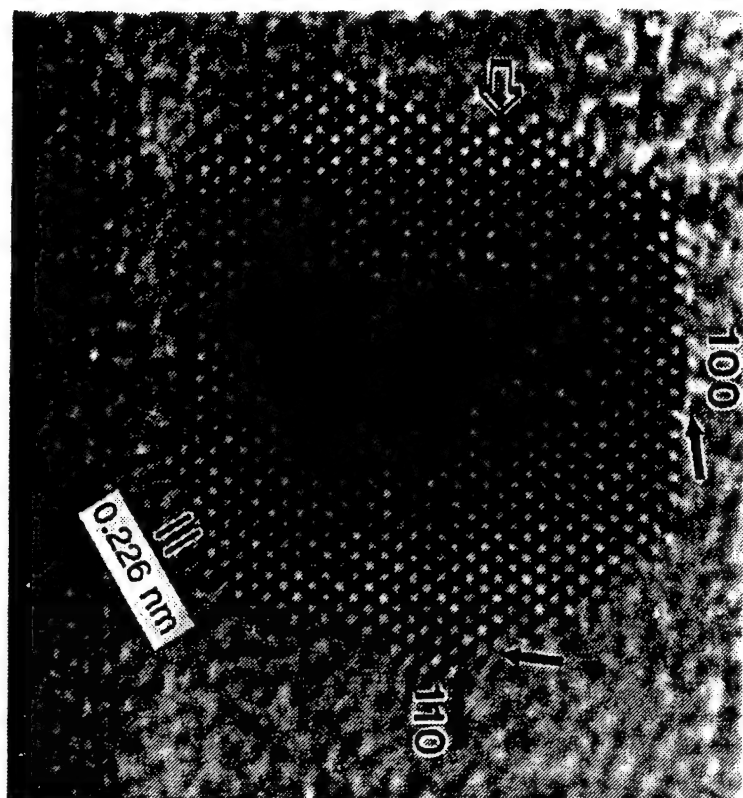
VG₄ THE DETAILED STRUCTURES OF INDIVIDUAL PLATINUM NANOCLUSTERS AT ATOMIC RESOLUTION: CUBIC ALONG [001]

A group of HRTEM images of cubic-like Pt particles oriented along [001], showing the presence of {110} facets, surface roughness, steps and ledges on the surfaces.



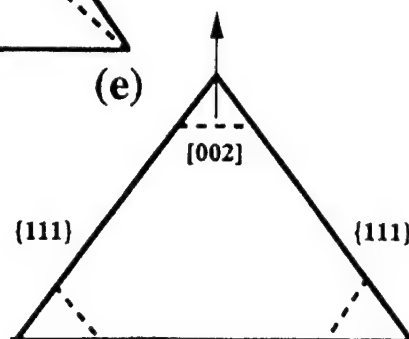
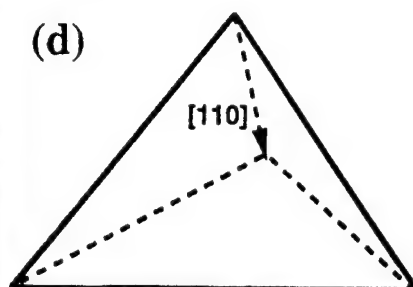
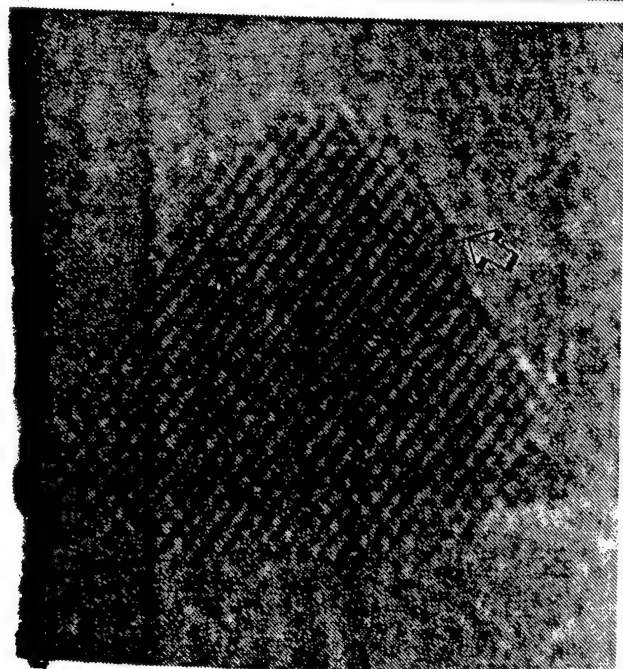
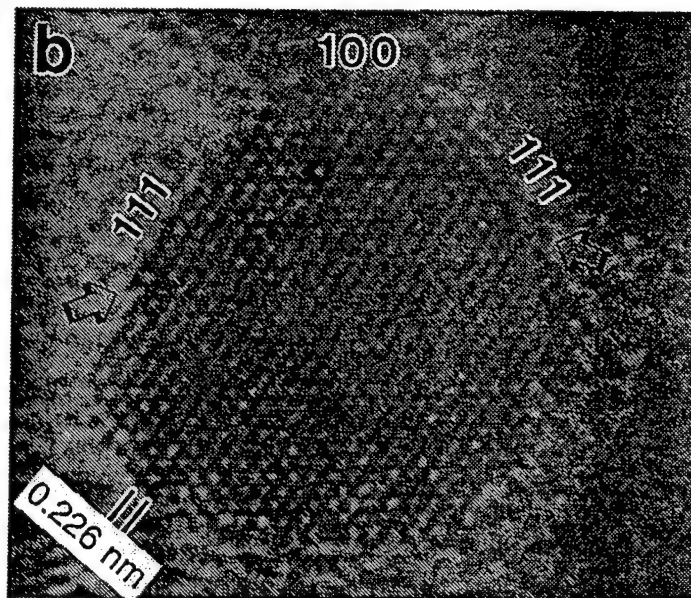
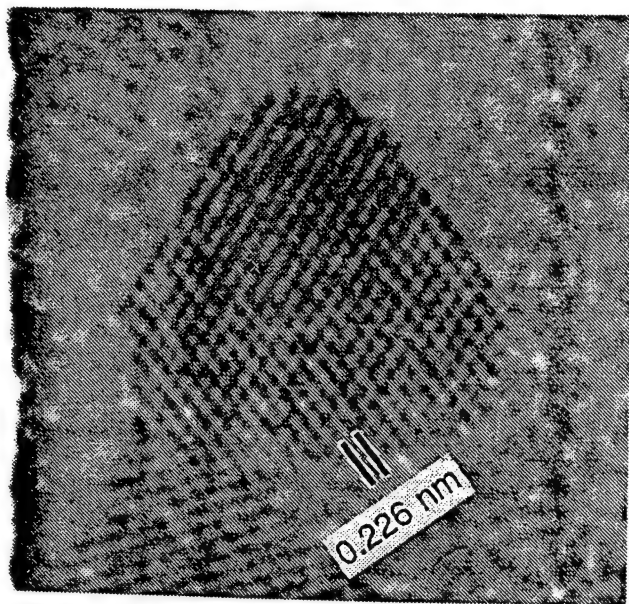
VG₅: THE DETAILED STRUCTURES OF INDIVIDUAL PLATINUM NANOCLUSTERS AT ATOMIC RESOLUTION: CUBIC ALONG [110]

A group of HRTEM images of cubic-like Pt particles oriented along [110], showing the presence of {111} facets, surface roughness on {110}, steps and ledges on {100}.



**VG₆: DETAILED STRUCTURES OF
INDIVIDUAL PLATINUM
NANOCLUSTERS AT ATOMIC
RESOLUTION: TETRAHEDRAL
ALONG [110]**

(a-c) A group of HRTEM images of tetrahedral-like Pt particles oriented along [110], showing the truncated shapes. A 3D shape and its [110] projection of a perfect tetrahedron are given in (d) and (e), respectively.

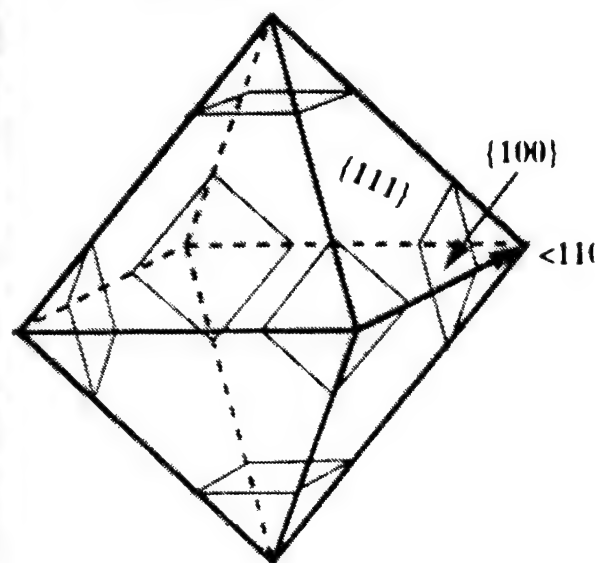


**VG₇: DETAILED STRUCTURE OF
INDIVIDUAL PLATINUM NANOCCLUSERS
AT ATOMIC RESOLUTION:
OCTAHEDRAL-LIKE**

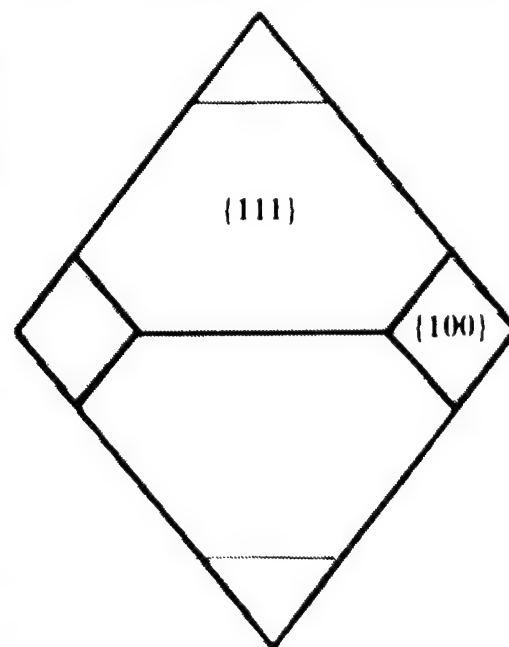
(a) A TEM image of octahedral-like Pt particles prepared by the shape-controlling technique. (b), (c) Schematic diagrams showing 3D and the [110] projection of a truncated octahedron.



(b) 3-D octahedron

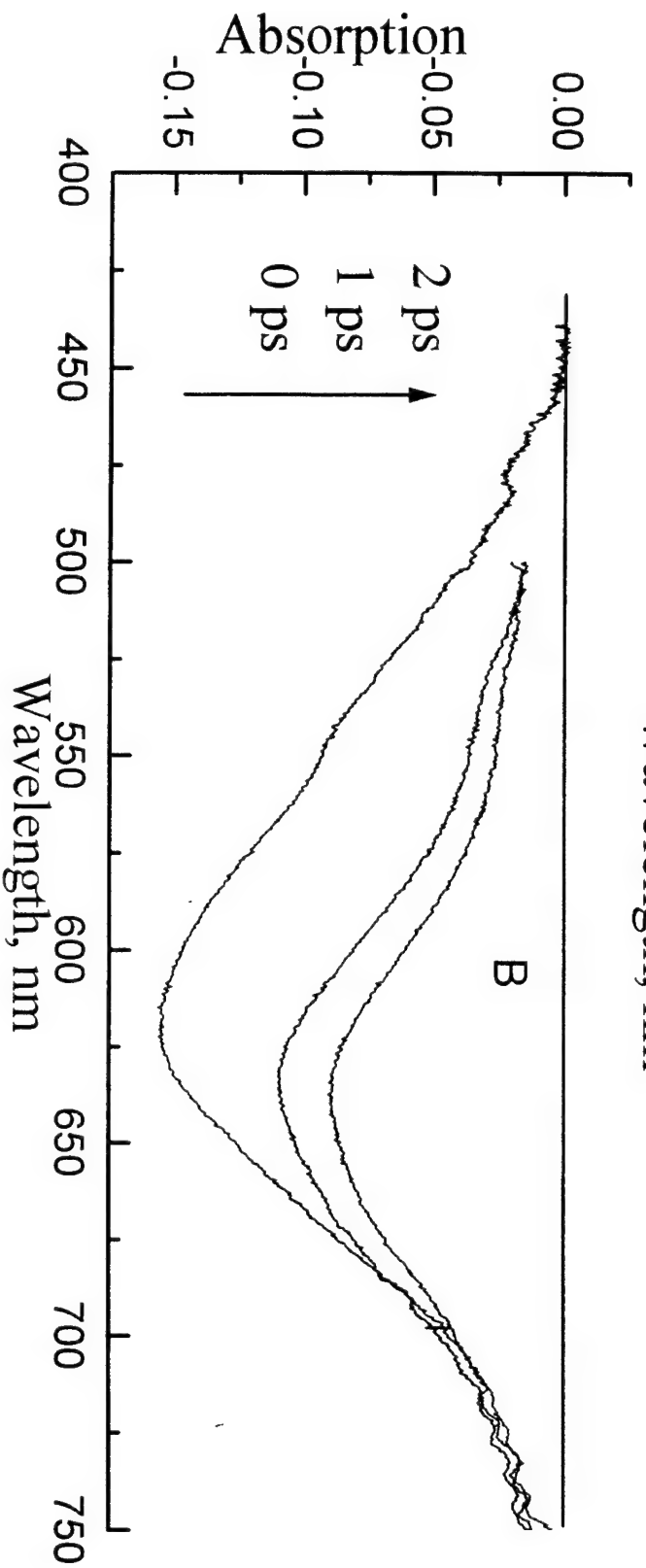
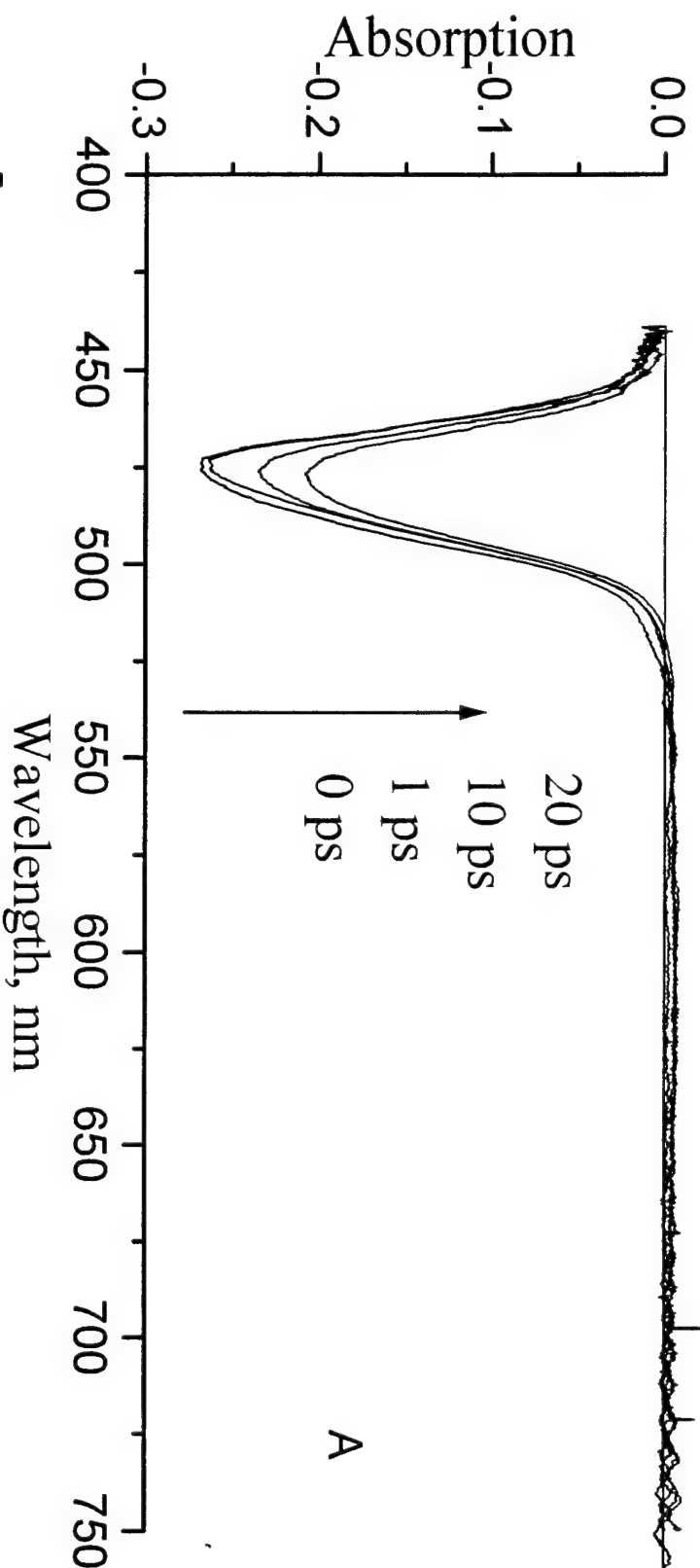


(c) $[110]$ projected octahedron



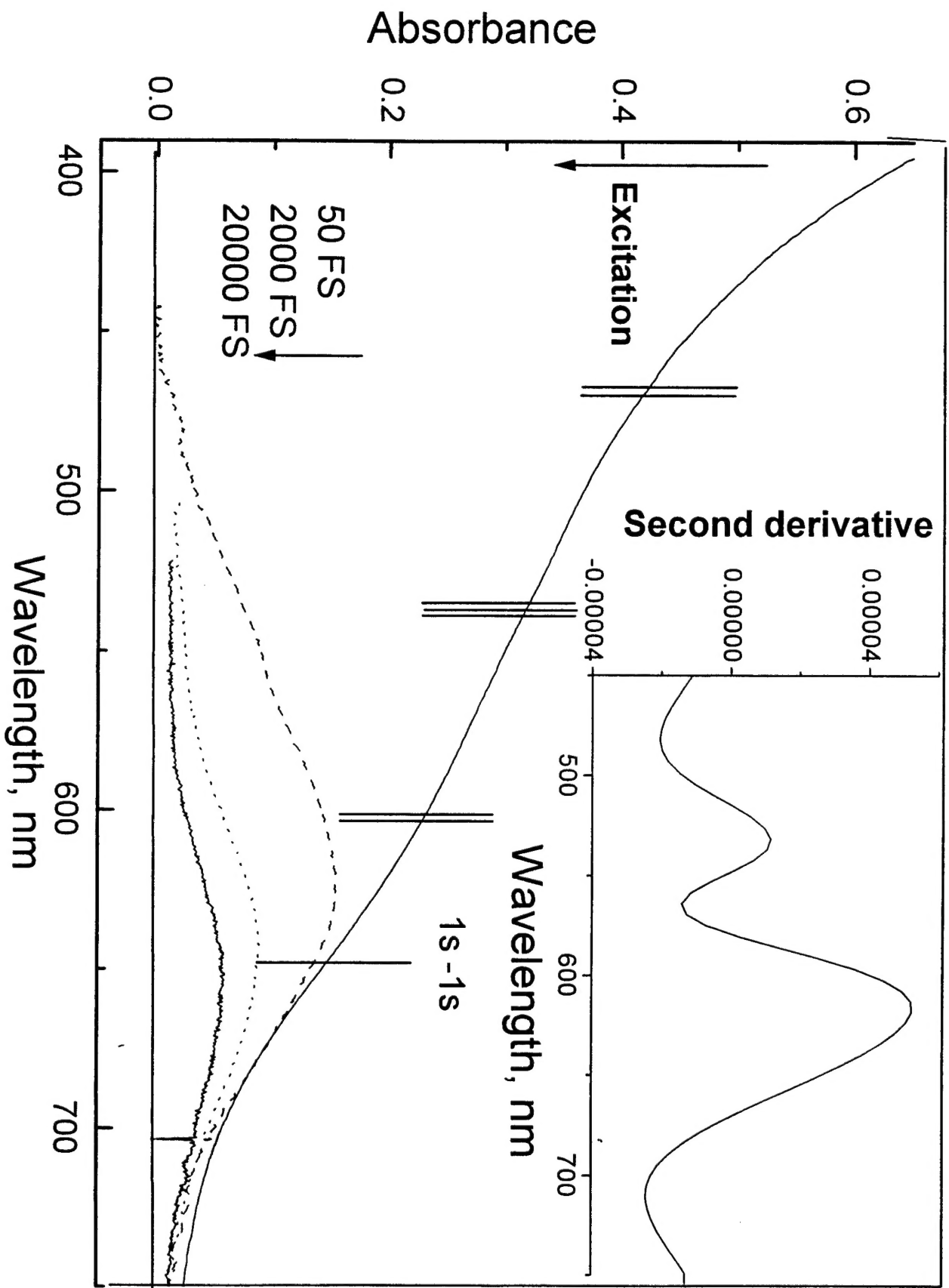
VG₈: TIME RESOLVED OPTICAL HOLE (OH) SPECTRA IN CDS QUANTUM DOTS AND CdS·HgS·CdS QUANTUM DOT QUANTUM WELL

The time dependence of the optical holes (oh) formed by pumping at 400 nm of the CdS quantum dot (QD) (top) and CdS·HgS·CdS quantum dot quantum well (QDQW) colloidal nanocrystals. Very rapid (<50fs) unresolved spectral diffusion in QD compared to the slower one (~ps) suggests that the presence of the well greatly reduces the nonradiative relaxation processes of the dot.



VG₉: RELAXATION BETWEEN EXCITED LEVELS RESPONSIBLE FOR SPECTRAL DIFFUSION IN CdS·HgS·CdS QDQW

Comparison of the Absorption Spectra (top) and Time dependence of the optical hole (bleach) spectra of the CdS·HgS·CdS quantum dot-quantum well colloidal nanocrystal. The vertical lines mark the calculated positions (Bryant, Phys.Rev) of the lowest eight optically active excitonic levels. The inset gives the derivative of the bleach spectrum at 50 fs delay (top broken-line spectrum). The correspondence between these two peaks and the energy level structure theoretically calculated suggested that spectral diffusion in this system results from relaxation involving the exciton levels of the QDQW nanoparticles.



VG₁₀: KINETIC SUPPORT OF RELAXATION MECHANISM IN CdS·HgS·CdS QDQW

The kinetics of formation (observed in the bottom figure) and decay (in the top spectrum) of the optical hole as monitored at the two different wavelength regions corresponding to the two peaks seen in the inset of VG₉. This suggested that the dynamics of the spectral diffusion in the QDQW nanoparticles has different kinetics in the two regions representing two different sets of energy levels predicted by theory. This supports the proposal that the spectral diffusion results from nonradiative relaxation between the exciton levels in this system.

Bleach intensity, arb. units

